

Molecular Layering of a Liquid at a Smooth Solid Surface

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Introduction

Lubrication, wetting, and biological and chemical processes are a few examples of situations where a change in the properties of liquids due to confinement has very significant implications. Recent experiments such as surface force and ellipsometry measurements and computer simulations [1-4] have indicated that there are structural changes in normal liquids within a few molecular dimensions of a solid-liquid interface. We have looked for direct and quantitative evidence of this using X-ray scattering.

Methods and Materials

We studied liquid films of tetrakis (2-ethylhexoxy) silane (TEHOS) on polished silicon substrates. TEHOS is almost completely non-volatile, and the molecules are roughly spherical, non-reactive and non-liquid-crystalline. In our initial studies [5], we made ultrathin (45-90Å) films of TEHOS by dipping silicon substrates in very dilute solutions and allowing the solvent to evaporate. However, such ultrathin films are very susceptible to surface-adsorbed impurities. Subsequently [6] we made thicker films by pouring pure TEHOS onto the silicon and draining it for an hour. The films show interference patterns in ambient light and the thickness is estimated to be $\sim 5000\text{\AA}$.

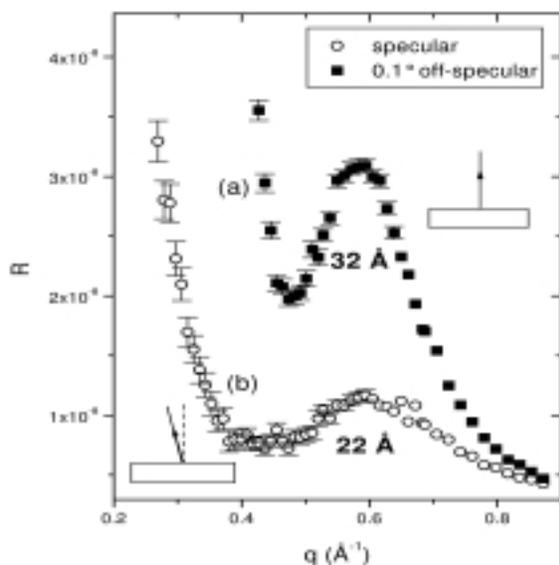


Fig 1. X-ray scattering from a $\sim 0.5\mu\text{m}$ liquid film of TEHOS on a clean, smooth ($\sim 3\text{\AA}$ FWHM) silicon substrate: (a) wave vector in the specular direction. (b) same sample but with wave vector at 0.1° to the specular direction. The peak in the specular direction is much stronger, and this is evidence of layer formation. [From ref. 6]

Results

Our initial work [5] using 45-90Å films showed evidence of molecular layering in the reflectivity data; however, this

evidence was partly obscured by the Kiessig fringes due to the overall thickness, and the ordering was adversely affected by impurities absorbed during the experiment.

Fig. 1(a) shows the scattering normal to a thicker ($\sim 5000\text{\AA}$) film of TEHOS on an Si substrate [6]. With no Kiessig fringes, a diffraction peak can be clearly seen. The correlation length is $\sim 32\text{\AA}$ and the spacing is comparable to the size of the molecule. The scattering in the off-specular direction also shows a peak, due to the isotropic correlations in the liquid, but it is much smaller and slightly wider.

It is not obvious from the data in Fig. 1 that the diffraction peak comes from layers at the solid-liquid interface. However, layering at the free surface of nonmetallic liquids has been looked for by others but never observed. Moreover, we have found that the diffraction peak cannot be seen when the Si surface is either rough or dirty. When a dirty substrate is used, the peak reappears after some hours, suggesting that the impurities diffuse away. All this is evidence that layering occurs at the solid-liquid interface.

Discussion

Part of the motivation for using ultrathin films in our initial studies [5] was the extensive surface force evidence of layering, seen in ultrathin films only. However, we have found that it is not necessary for the liquid to be doubly confined; layers are formed at a single solid-liquid interface.

We used TEHOS for these experiments because it evaporates very slowly [2], but there is no reason to believe that it is otherwise a special case. We plan to show with further studies that there is significant layering in many liquids near a hard wall. We hope that such information will help in explaining and predicting the static and dynamic properties of liquids near interfaces and in the form of thin films.

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